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# **DURIP: ACQUISITION OF A LIQUID-CHROMATOGRAPHY / MASS-SPECTROMETRY SYSTEM.**

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## **LONG-TERM GOALS:**

My primary research interest is the effect of phytoplankton community structure on carbon cycling and optical properties of the marine environment. Methods used in our lab are based on biomarkers - chlorophylls, carotenoids, and sterols - to study marine phytoplankton communities and their effects on carbon cycling in the ocean and ocean optics. It is my intent to contribute with these studies to the understanding of the factors that govern these processes in the ocean. I intend to continue water column studies in the Southern California Bight and to start a program in the Eastern Tropical Pacific to study the interaction of phytoplankton physiology, water column structure and subsurface oxygen concentrations. In parallel, I will study phytoplankton-derived chromophores in the marine environment, characterized these, determine their effects on ocean optics and assess their utility as biomarker for the study of phytoplankton in the ocean.

## **OBJECTIVES:**

The objective of the award is to purchase an liquid-chromatography/mass-spectroscopy (LC/MS) system for the characterization and analysis of biomarkers isolated from the marine environment.

## **WORK COMPLETED:**

We purchased a Finnigan LCQ ion-trap mass-spectrometer with an electrospray (ESI) and atmospheric pressure chemical ionization (APCI) source and a Shimadzu binary high-pressure-mixing LC system capable of solvent delivery at low flow rates with a UV/Vis detector. The system was set up in a newly renovated laboratory in July/August. The integration of the LC with the MS system was achieved. So far we have developed methods for the LC/MS analysis of chlorophyll degradation products and carotenoids in extracts of sediment and water column particulate samples. We have isolated or synthesized a range of standards and have subjected these to MS and MS<sup>n</sup> analysis to characterize the response of these compounds to the different ionization methods and to ion-trap fragmentation. A range of samples was subjected to preliminary analysis as well.

## **RESULTS:**

We have set up an LC/MS facility that is currently being used by a variety of scientists at SIO for the analysis of pigments, sterols, microsporin amino acids and pharmaceutically active natural products. My group has used the instrument to analyze novel chromophores isolated from sediments and pigments associated with a strain of *Prochlorococcus sp.* that is found in the upper part of the oxygen minimum of the Arabian Sea and the Eastern Tropical North Pacific. In sediments we discovered esters of the chlorins pheophorbide a and pyropheophorbide and the carotenoids (iso)fucoxanthin-5'-dehydrate and (iso)fucoxanthiol-5'-dehydrate; compounds that we believe to be biomarkers for the grazing of copepods on diatoms. The analysis of the pigments of *Prochlorococcus* confirmed our previous identifications and revealed the possible presence of large concentrations of b-cryptoxanthin-5,8-epoxide in this strain when grown under low light conditions.

## **IMPACT:**

The availability of an LC/MS system at Scripps has greatly increased our analytical capabilities. In particular it now allows us to unambiguously identify the compounds we routinely analyze by HPLC as part of other programs.

## **RELATED PROJECTS:**

Our LC/MS system will benefit a range of programs at Scripps: Pigment-identifications carried out on the system will benefit my NSF-sponsored work in the Arabian Sea and the Eastern Tropical North Pacific. Work proposed to ONR, a study of detrital chromophores and their impact on ocean optics, relies on the availability of an LC/MS system.